PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's A02-4001	-	ent's file reference	FOR FURTHER ACTIO	~~1	cation of Transmittal of International y Examination Report (Form PCT/IPEA/416)
Internationa			International filing date (day/	month/year)	Priority date (day/month/year)
PCT/NL0	2/00	119	22/02/2002		22/02/2001
International C07C2/3		ent Classification (IPC) or nat	tional classification and IPC		
Applicant					
STICHTII	NG E	DUTCH POLYMER INS	STITUTE et al.		
		ational preliminary exami smitted to the applicant a		pared by this Inte	ernational Preliminary Examining Authority
2. This F	REPC	ORT consists of a total of	4 sheets, including this co	ver sheet.	
be	een a	mended and are the bas		ets containing re	on, claims and/or drawings which have ectifications made before this Authority he PCT).
These	ann	exes consist of a total of	6 sheets.		
3. This re	eport	contains indications rela	ting to the following items:		
1	☒	Basis of the report			•
B					
111		Non-establishment of o	pinion with regard to novelt	y, inventive step	and industrial applicability
IV		Lack of unity of invention	n		
V	☒		nder Article 35(2) with regar		entive step or industrial applicability;
VI		Certain documents cite	ed		
VII		Certain defects in the in	ternational application		
VIII		Certain observations or	the international application	on	
					<u> </u>
Date of sub	missio	on of the demand	Da	te of completion of	this report
18/09/200	02		21	.05.2003	
		g address of the international Ining authority:	I Au	thorized officer	SEPTICOES MOVING.
<u>)</u>	D-80 Tel.	opean Patent Office 0298 Munich +49 89 2399 - 0 Tx: 523656 : +49 89 2399 - 4465	epmu d	oetz, G lephone No. +49 8	0 2200 8105

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL02/00119

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	1.	Bas	is f the report							
	1.	With regard to the elements of the international application (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)): Description, pages:								
		1-4	6-20	as originally filed						
		5,5	a	as received on	10/03/2003	with letter of	10/03/2003			
		Cla	ims, No.:				·			
		1-2	0	as received on	10/03/2003	with letter of	10/03/2003.			
	2.			guage, all the elements ma international application w						
		These elements were available or furnished to this Authority in the following language: , which is:								
		☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).								
			the language of pu	ublication of the internation	nal application (und	er Rule 48.3(b)).				
			the language of a 55.2 and/or 55.3).	translation fumished for th	ne purposes of inter	national preliminar	y examination (under Rule			
	3.		•	cleotide and/or amino ac ry examination was carried	•		• •			
l			contained in the in	itemational application in v	written form.					
			filed together with	the international application	on in computer read	lable form.				
			furnished subsequ	ently to this Authority in w	ritten form.					
			furnished subsequ	ently to this Authority in c	omputer readable fo	orm.				
				it the subsequently furnish pplication as filed has bee	•	e listing does not g	o beyond the disclosure in			
			The statement that listing has been full	t the information recorded irnished.	l in computer readal	ble form is identica	I to the written sequence			
	4.	The	amendments have	e resulted in the cancellation	on of:					
			the description,	pages:						
			the claims,	Nos.:						
			the drawings,	sheets:						

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INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/NL02/00119

5.	This report has been established as if (some of) the amendments had not been made, since the	ney have been
	considered to go beyond the disclosure as filed (Rule 70.2(c)):	

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

- 6. Additional observations, if necessary:
- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Novelty (N)

Yes: No:

Claims 1,3-14

Inventive step (IS)

Yes:

Claims 15-20 Claims 1,3-14

No: Claims

Industrial applicability (IA)

Yes: Claims 1,3-20 No: Claims

2. Citations and explanations see separate sheet

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Re It m V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

D1: EP-A-0608447

D2: Journal Of Organometallic Chemistry, Elsevier-sequoia S.a. Lausanne,

Ch (1999), 592, 84-94

D3: WO-A-9425416

Present claim 2 as well as the amendment on page 5 does not meet the 1. requirements of Article 19(2) PCT: there is no basis to be found in the application as filed for a "pressure from 0,2 to 14 MPa".

2. The catalyst system used in the trimerization process is known from D2 (as already acknowledged from the applicant in the description).

A catalyst is not rendered novel by the mere fact that this catalyst may be used in a novel process.

Present claims 15 to 20 are thus not novel over the prior art disclosed in D2 (PCT Article 33.2).

- 3 The claimed trimerization process according to claims 1 and 14 is not disclosed in any of the available prior art documents D1 to D3).
 - The subject matter of present claims 1, 3 to 14 is thus considered to be novel over said prior art (PCT Article 33.2).
- 4. There is no hint to be found in any of the prior art documents that the catalyst system known from D2 could be used in the trimerization of olefinic compounds according to present claims 1, 3 14.
 - In particular the disclosure of D2 leads away from such a use of the known catalyst system since it is indicated in D2 (see page 89 left column) that the catalyst system used in D2 leads to polymer products.
 - The subject matter of present claims 1, 3 to 14 is thus regarded to be based on an inventive step (PCT Article 33.3)
- 3. The industrial applicability is given for all claims examined (Article 33.4 PCT)

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that any activator can be used provided that it is abl to generate a cationic transition metal species with a non-coordinating anion. The term "non-coordinating anion" is meant to indicate the anionic part or derivative of the activator, which not or only weakly coordinates to the cationic form of the present catalyst system.

Preferably the activator is methylalumoxane (also known as MAO). The molar ratio of Ti:Al is expediently from 1:100 to 1:1000.

The present catalyst system can further also comprise a scavenger. Examples of a scavenger are i-Bu₃Al and (i-Bu₂Al)₂O. A scavenger is normally used to scavenge impurities from a polymerisation medium to obtain a high productivity.

The invention further relates to a process to trimerize olefinic compounds which comprises carrying out said trimerisation in the presence of a catalyst system, as described above, under trimerisation conditions. Such a trimerisation als comprises cotrimerisation according to the definition given before.

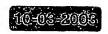
The olefin to be trimerized is preferably selected from C_2 - C_{20} olefins or mixtures of two or more of these olefins. The preferred olefins are ethylene and 1-butene, more preferably ethylene.

The temperature is preferably in the range of from 20-150°C, at a pressure which is commonly in the range from 0,2 to 14 MPa, preferably in the range of from 1,5 to 3 MPa.

The invention will further be explained in the following examples.

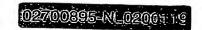
Experimental section General considerations

All experiments were performed under a nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Na/K alloy and vacuum transferred before use. Cyclooctane (Aldrich, used as internal standard) was distilled from Na prior to use. Toluene (Aldrich, anhydrous, 99,8%) was passed over columns of Al₂O₃ (Fluka), BASF R3-11 supported Cu oxygen and molecular sieves (Aldrich, 4Å). Diethyl ether and THF (Aldrich) were dried over Al₂O₃ (Fluka) and the other solvents (Aldrich) were dried over molecular si ves (Aldrich, 4Å). Ethene





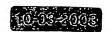




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(AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scav nger and molecular sieves (Aldrich, 4Å).

The compounds 6,6-p ntamethyl nefulvene, C₅H₅CH₂Ph, (C₅H₄C(=CH₂)Ph)Li, (C₅H₄CMe₂Ph)TiCl₃ (th catalyst us d in



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NEW CLAIMS

- 1. A process for the selective trim rization of olefinic compounds under trimerization conditions in the presence of a catalyst system, characterized in that said process is effected by using a catalyst system which comprises
- 5 A) a cyclopentadienyl titanium complex of formula $(Cp-B(R)_nAr) \text{Ti} R^1 3$

wherein

Cp is a cyclopentadienyl type ligand, optionally being substituted,

- B is a bridging group, based on a single atom selected from the groups 13 to 16 inclusive of the Periodic System,
- Ar is a aromatic group, optionally substituted,
- R is, independently, hydrogen, or a hydrocarbon residue, optionally being substituted and optionally containing heteroatoms, or groups R and B are joined together to form a ring,
- n is an integer equal to the (valency of B minus 2), and \mathbb{R}^1 is a mono-anionic group, and
- B) an activator,
- and wherein said olefinic compounds are selected from C_2-C_{20} olefines and mixtures of two or more of these olefins.
- A process according to claim 1, wherein said process is effected at a temperature from 20-150°C, at a pressure from 0,2 to 14
 MPa, preferably 1,5 to 3 MPa.
 - 3. A process according to any of the claims 1 or 2, wherein the single atom forming the basis of group B is selected from B, C, N, O, Si, P and S.
 - 4. A process according to any of the claims 1 to 3 wherein the single atom forming the basis of said group B consists of carbon or silicon,

Ar is phenyl, optionally substituted or being part of a larger



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aromatic ntity,

- R¹ is a halogen atom, or mono-anionic hydrocarbon r sidu optionally containing heteroatoms, and
- n is 2, then R is a mono-anionic hydrocarbon residue, optionally containing heteroatoms, or
- n is 1, then R is a di-anionic hydrocarbon residue, optionally containing heteroatoms.
- 5. A process according to any of the claims 1 to 4, wherein Cp
 is a cyclopentadienyl type ligand being substituted, besides said
 B-(R)n group, with 1 to 8 groups of formula -YR2R3R4 in which Y is C
 or Si and R2, R3 and R4 are, independently, H, halogen, lower alkyl,
 aryl, lower-alkyl-aryl, aryl-lower alkyl residue, wherein said alkyl
 and aryl are independently substituted or not with one or more lower
 alkyl residues, said alkyl and aryl residues being independently
 provided or not with at least one heteroatom, selected from halogen,
 nitrogen, oxygen, sulfur and phosphor.
- 6. A process according to any of the claims 1 to 5, wherein 20 said lower alkyl residues, being the same or different to each other, are linear or branched C₁-C₅ alkyl residues, more specifically methyl.
- 7. A process according to any of the claims 1 to 6, wherein 25 said aryl group in the alkylaryl or arylalkyl residue is a phenyl group.
 - 8. A process according to any of the claims 4 or 5, wherein said halogen is fluorine or chlorine.
 - 9. A process according to any of the claims 1 to 8, wherein Ar is a phenyl group, substituted or not at the meta-or paraposition,
 - B is based on a carbon atom,
- 35 n is 2, th n groups R are, independently, methyl, or ethyl; or
 - n is 1, then group R is = CH_2 , or forms when R is C_4H_8 or C_5H_{10}



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tog ther with group B a dianionic cyclic group Cp is C_5H_4 or $C_5H_3(SiMe_3)$, or $C_5H_3(CMe_2Ph)$, and R^1 is chlorin , methyl, or benzyl.

- 5 10. A process according to any of the claims 1 to 9, wherein said titanium complex is supported on a carrier.
- 11. A process according to any of the claims 1 to 10, wherein said activator is methylalumoxane, a salt of a non-coordinating anion, or a Lewis acid capable of abstracting an anion from said transition metal complex.
 - 12. A process according to claim 11 wherein the activator is methylalumoxane and the molar ratio of Ti:Al is from 1:100 to 1:1000.
 - 13. A process according to any of the claims 1 to 12, wherein said catalyst system further comprises a scavenger.
- 14. A process according to claim 13, wherein said scavenger is selected from i-Bu₃Al and (i-Bu₂Al)₂O.
 - 15. A catalyst system for the selective trimerization of olefins, characterized in that said catalyst system comprises
- A) a half-sandwich substituted cyclopentadienyl titanium complex of formula

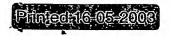
 $(Cp-B(R)_nAr)TiR^1_3$

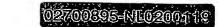
wherein

- Cp is a cyclopentadienyl type ligand, optinally substituted,
- B is a bridging group, based on a single atom selected from the groups 13 to 16 inclusive of the Periodic System,
- Ar is a aromatic group, optionally substituted,
- R is, independently, hydrogen, or a hydrocarbon residue, optionally being substituted and optionally containing heteroatoms, or groups R and B are joined together to form
- 35 a ring,



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- n is an int ger qual to th (val ncy of B minus 2), and ${\bf R}^{\bf 1}$ is a mono-anionic group, and
- b) an activator.
- 16. A catalyst system according to claim 15, wherein the singl atom forming the basis of group B is selected from B, C, N, O, Si, P and S.
- 17. A catalyst system according to any of the claims 15 or 16

 10 wherein the single atom forming the basis of said group B consists of carbon or silicon,
 - Ar is phenyl, optionally substituted or being part of a larger aromatic entity,
- R¹ is a halogen atom, or mono-anionic hydrocarbon residue optionally containing heteroatoms, and
 - n is 2, then R is a mono-anionic hydrocarbon residue, optionally containing heteroatoms, or
 - n is 1, then R is a di-anionic hydrocarbon residue, optionally containing heteroatoms.

18. A catalyst system according to any of the claims 15 to 17, wherein Cp is a cyclopentadienyl type ligand being substituted, besides said B-(R)n group, with 1 to 8 groups of formula -YR2R3R4 in which Y is C or Si and R2, R3 and R4 are, independently, H, halogen, lower alkyl, aryl, lower-alkyl-aryl, aryl-lower alkyl residue, wherein said alkyl and aryl are independently substituted or not with one or more lower alkyl residues, said alkyl and aryl residues being independently provided or not with at least one heteroatom, selected from halogen, nitrogen, oxygen, sulfur and phosphor.

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19. A catalyst system according to any of the claims 15 to 18, wherein said lower alkyl residues, being the same or different to each other, ar linear or branched C_1 - C_5 alkyl r sidues, mor specifically methyl.

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20. A catalyst system according to any of the claims 15 to 19,



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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER see Notification o	f Transmittal of International Search Report 20) as well as, where applicable, item 5 below.
A02-40015/TK	ACTION (POINT PC 1715A/2)	20) as well as, where applicable, item 5 below.
International application No.	International filing date (day/month/year)	(Earliest) Priority Date (day/month/year)
PCT/NL 02/00119	22/02/2002	22/02/2001
Applicant		
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STICHTING DUTCH POLYMER I	NSTITUTE	
This International Search Report has bee according to Article 18. A copy is being to	n prepared by this International Searching Autransmitted to the International Bureau.	nority and is transmitted to the applicant
	-	
This International Search Report consists It is also accompanied by	of a total of sheets. a copy of each prior art document cited in this	report.
1. Basis of the report		
	international search was carried out on the bas less otherwise indicated under this item.	sis of the international application in the
the international search v Authority (Rule 23.1(b)).	vas carried out on the basis of a translation of t	he international application furnished to this
b. With regard to any nucleotide ar was carried out on the basis of the	nd/or amino acid sequence disclosed in the in	ternational application, the international search
1	e sequence listing : onal application in written form.	
filed together with the into	ernational application in computer readable for	n.
furnished subsequently to	this Authority in written form.	
furnished subsequently to	this Authority in computer readble form.	
the statement that the su international application a	bsequently furnished written sequence listing das filed has been furnished.	oes not go beyond the disclosure in the
the statement that the inf furnished	ormation recorded in computer readable form i	s identical to the written sequence listing has been
2. Certain claims were fou	and unsearchable (See Box I).	
3. Unity of invention is lac	eking (see Box II).	
4. With regard to the title ,		
X the text is approved as s	ubmitted by the applicant.	
the text has been establi	shed by this Authority to read as follows:	
5. With regard to the abstract,		
the text has been establi	ubmitted by the applicant. shed, according to Rule 38.2(b), by this Author e date of mailing of this international search re	
6. The figure of the drawings to be put	olished with the abstract is Figure No.	
as suggested by the app	licant.	X None of the figures.
because the applicant fa	iled to suggest a figure.	_
because this figure bette	r characterizes the invention.	

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INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 02/00119

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C2/32 B01J31/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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 $\begin{array}{ccc} \text{Minimum documentation searched (classification system followed by classification symbols)} \\ IPC & 7 & C07C & B01J \end{array}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to daim No.
A	EP 0 608 447 A (PHILLIPS PETROLEUM CO) 3 August 1994 (1994-08-03) cited in the application claims 20-24	14,15
X	SASSMANNSHAUSEN J ET AL: "HALF-SANDWICH COMPLEXES OF TITANIUM AND ZIRCONIUM WITH PENDANT PHENYL SUBSTITUENTS. THE INFLUENCE OF ANSA-ARYL COORDINATION ON THEPOLYMERISATION ACTIVITY OF HALF-SANDWICH CATALYSTS" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 592, 1999, pages 84-94, XP001033815 ISSN: 0022-328X cited in the application table 1	1-13

X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.
 Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed 	 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combined with one or more other such documents, such combination being obvious to a person skilled in the art. '&' document member of the same patent family
Date of the actual completion of the international search 22 April 2002	Date of mailing of the international search report 29/04/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.	Authorized officer
Fax: (+31-70) 340-3016	Goetz, G

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 02/00119

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
4	WO 94 25416 A (SHELL INT RESEARCH) 10 November 1994 (1994-11-10) page 2, line 14 -page 3, line 4	14,15
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 02/00119

cited in search report		Publication date		Patent family member(s)	Publication date
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			CA	2087578 A1	20-07-1994
			CZ	9300088 A3	17-08-1994
				3188335 B2	16-07-2001
			JP	6239920 A	30-08-1994
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			EP	0608447 A1	03-08-1994
			AT	207084 T	15-11-2001
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					11-02-2002
			ES	2161699 T3	16-12-2001
WO 9425416	A	10-11-1994	AU	683060 B2	30-10-1997
			AU	6650394 A	21-11-1994
			BR	9406460 A	30-01-1996
•				2161664 A1	10-11-1994
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				9502826 A3	15-05-1996
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					14-02-1996
				955104 A	26-10-1995
					08-10-1996
			NO	954292 A	26-10-1995
	EP 0608447	EP 0608447 A	EP 0608447 A 03-08-1994	EP 0608447 A 03-08-1994 AU CA CZ JP JP NO EP AT DE DE DK ES	EP 0608447 A 03-08-1994 AU 650808 A1 CA 2087578 A1 CZ 9300088 A3 JP 3188335 B2 JP 6239920 A NO 930340 A EP 0608447 A1 AT 207084 T DE 69330943 D1 DE 69330943 T2 DK 608447 T3 ES 2161699 T3 WO 9425416 A 10-11-1994 AU 683060 B2 AU 6650394 A BR 9406460 A CA 2161664 A1 CN 1121704 A , B CZ 9502826 A3 DE 69405222 D1 DE 69405222 D1 DE 69405222 T2 DK 696263 T3 WO 9425416 A1 EP 0696263 A1 FI 955104 A JP 8509518 T

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